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PATENT & TRADEMARK OFFICE

KRATON™ Polymers

August 11, 2005

Via First Class Mail

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Re: U.S. Patent Application Serial No. 10/508,909 for "Poly (Styrene-Butadiene-Styrene) Polymers Having a High Vinyl Content in the Butadiene Block and Hot Melt Adhesive Compositions Comprising Said Polymers"
Applicant(s): Geert E. A. Vermunicht, et al.
Filing Date: September 23, 2004
Attorney Docket No.: TS6632/US

Dear Sir:

Please find the following enclosed documents:

1. Claim to Priority;
2. Certified Copy of EP 02076178.9 filed March 26, 2002; and
3. Return Receipt Postcard.

The Commissioner is hereby authorized to charge and credit KRATON Polymers U.S. LLC Deposit Account No. 50-1951 for the fees necessitated with the filing of this correspondence.

Respectfully submitted,

Donna B. Holguin
Intellectual Property Patent Attorney

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OIPE JC109 AUG 15 2005 PATENT & TRADEMARK OFFICE

Attorney Docket No. TS6632/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Geert E. A. Vermunicht, et al.	§	
	§	Group Art Unit: 1713
Application Serial No.: 10/508,909	§	
	§	Examiner: Ives J. Wu
Filing Date: September 23, 2004	§	
	§	
Title: Poly(Styrene-Butadiene-Styrene) Polymers Having a High Vinyl Content in the Butadiene Block and Hot Melt Adhesive Compositions Comprising Said Polymers	§	Attorney Docket No.: TS6632/US

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Certificate of Mailing
37 CFR 1.8
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8/11/05 (Date) Signature

Dear Sirs:

CLAIM TO PRIORITY

Applicant(s) reaffirm the claim for the benefit of the filing date of the following patent application referred to in Applicants' Declaration:

European application Serial No. 02076178.9 filed March 26, 2002.

A copy of the application certified by the European Patent Office is enclosed.

The Commissioner is hereby authorized to charge any fees necessitated with the filing of this correspondence to Deposit Account 50-1951 TS6632/US

Respectfully submitted,

Date: August 11, 2005

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Europäisches Patentamt	European Patent Office	Office européen des brevets

Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02076178.9

CERTIFIED COPY OF PRIORITY DOCUMENT

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Europäisches Patentamt | European Patent Office | Office européen des brevets

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Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

02076178.9

CERTIFIED COPY OF PRIORITY DOCUMENT

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Anmeldung Nr:
Application no.: 02076178.9
Demande no:

Anmeldetag:
Date of filing: 26.03.02
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Poly (styrene-butadiene-styrene) polymers having a high vinyl content in the butadiene block and hot melt adhesive composition comprising said polymers

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
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POLY(STYRENE-BUTADIENE-STYRENE) POLYMERS HAVING A HIGH VINYL CONTENT IN THE BUTADIENE BLOCK AND HOT MELT ADHESIVE COMPOSITION COMPRISING SAID POLYMERS

Summary of the invention

The present invention comprises a poly(styrene-butadiene-styrene) polymer having a high vinyl content in the butadiene block for packaging tape adhesives and a hot melt polymer adhesive composition comprising said poly(styrene-butadiene-styrene) polymers (SvBS).

More particularly the present invention concerns a hot melt adhesive composition having equal or better properties compared to emulsion acrylic tapes. The adhesive composition of the present invention has excellent tack, adhesive strength, creep resistance and also an excellent treatment capability at high temperature and high box closing properties.

The adhesives of the present invention are suitable for adhesion tapes, labels, pressure sensitive sheets, tacky adhesives for fixing carpets etc.

The advantages of the adhesives of the present invention are that they are lower in cost compared to emulsion acrylic

based adhesives or poly(styrene-isoprene-styrene) based adhesives (SIS) while having comparable or better properties.

Background of the Invention

Hot melt adhesives are known, for instance, in the JP 2001787 describing tacky adhesive compositions for tapes comprising a block copolymer of a vinylaromatic hydrocarbon and a high vinyl polybutadiene block. The composition comprises a block copolymer, a tackifying resin and at least one phenol compound. The block copolymer is composed of at least one polymeric block mainly containing butadiene. It has a vinylaromatic hydrocarbon content of 10-36% by weight and the butadiene portions have a vinyl content of 15-55%.

The JP 63182386 discloses sticky block copolymer compositions containing a vinyl aromatic-butadiene block copolymer, a tackifying resin and a phenolic compound. The block copolymer is mainly composed of vinyl aromatic hydrocarbon and at least one polymer block composed of polybutadiene.

The EP-A-0 243 956 discloses an adhesive composition comprising a block copolymer containing at least one vinylaromatic hydrocarbon block and one butadiene containing block, wherein the relationship between the vinylaromatic hydrocarbon block and the 1,2-vinyl content in the butadiene portion is within a ratio between 40 and 70. In addition, the polymers that have been used have a melt flow rate of 5g/10min (200°C, 5kg).

These hot melt compositions however do not have the same properties as those based on SIS in respect of the tack, adhesive strength creep resistance and treatment capacity at high temperature as well as high box closing properties.

The object of the invention is a hot melt adhesive composition having equal or better properties compared to prior art adhesives, especially the acrylic emulsion based adhesives while being cheaper than poly(styrene-isoprene-styrene) (SIS) based adhesives.

Poly(styrene-isoprene-styrene) polymers are currently rarely used in pressure sensitive adhesives despite their relative low cost. The main reason for this is their high viscosity and tendency to cross-link so that the processing step becomes a limiting factor. Surprisingly a new SBS polymer has been developed with molecular parameters suitable for to hot melt adhesive applications.

Brief description of the invention

Accordingly, the inventors have provided a poly(styrene-butadiene-styrene) polymer having a high vinyl content in the butadiene block comprising in combination :

i) a polystyrene content (PSC) within a range of 15-20% by weight,
ii) a coupling efficiency of 50-80%,
iii) a step I (MW) between 9000 and 10000 kg/mol
iv) a vinyl content between about 20-45% by weight.

Further the inventors have provided a hot melt adhesive composition comprising:

a) a poly(styrene-butadiene-styrene) polymer having a high vinyl content in the butadiene block
b) a tackifying resin
c) a plasticizer
d) an anti-oxidant

wherein said polymer has :

i) a polystyrene content (PSC) within a range of 15-20% by weight,
ii) a coupling efficiency (CE) of 50-80%,
iii) a step I (MW) between 9000 and 10000 kg/mol

iv) a vinyl content between about 20-45% by weight.

Detailed description of the invention

Preferred poly(styrene-butadiene-styrene) polymers having a high vinyl content in the butadiene block have a polystyrene content between 16-19% by weight, more preferably 16-18%. Likewise the preferred polymers have a coupling efficiency between 60-75%, more preferably 65-70%. Moreover the preferred polymers have a vinyl content between 25-40% by weight, more preferably 30-35.

A suitable embodiment of the present invention is defined as follows:

PSC content (%)	16
CE (%)	67
vinyl (%)	33,6
Step I (MW) (kg/mol)	9,100

According to another embodiment of the present invention the polymer is defined as follows:

PSC content (%)	18
CE (%)	67
vinyl (%)	32
Step I (MW) (kg/mol)	9,100

Suitable styrenes useful for preparing the polystyrene blocks of the SvBS of the present invention are for example styrene, o-methylstyrene, p-methylstyrene, m-methylstyrene, p-tert-butylstyrene, dimethylstyrene, and various other alkyl-substituted styrenes, alkoxy-substituted styrenes vinylnaphthalene and vinyl xylene. The alkyl and alkoxy groups of the alkyl-substituted or alkoxy substituted styrenes respectively preferably contain from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms. It is to be noticed that this list is merely illustrative and should not have a limiting

effect. The polystyrene blocks may comprise minor amounts (e.g. up to 5 % by weight) of copolymerizable monomers.

In the preparation of the polymers according to the invention any suitable difunctional coupling agent can be used. Alternatively, the same polymer may be produced by what is called "full sequential". This is also within the scope of this invention.

The coupling agent may (not preferred) be a multifunctional coupling agent. Suitable coupling agents are dibromo ethane diglycidyl ether of bisphenol A and such like components as known in the art.

Suitable tackifiers for preparing the hot melt adhesive composition of the present invention are well-known in the art. They may for example,be selected from the group consisting of compatible C_5 hydrocarbon resins, hydrogenated C_5 hydrocarbon resins, styrenated C_5 resins, C_5/C_9 resins, styrenated terpene resins, fully hydrogenated or partially hydrogenated C_9 hydrocarbon resins, rosins esters, rosins derivatives and mixtures thereof.

The composition according to the present invention preferably comprises from 50 to 200 parts by weight, more preferably from 100 to 150 parts by weight of a tackifier.

The preferred tackifying resins useful in the present invention are selected within the group of HERCOTAC 205 (trademark), an aromatic modified hydrocarbon resin of the Hercules grade range, used for natural rubber based packaging tapes; PICCOTAC 212 (trademark) a purely aliphatic resin widely used in hot melt pressure sensitive adhesives; MBG 223,a Hercules development grade which is a 35% aromatic modified C_5 resin, developed for tackifying SBS based adhesives; MBG 264,a partially hydrogenated hydrocarbon resin used in radiation curable adhesives based on SBS; and A 2514 which is a liquid developmental resin, with a very low softening point to be used

in combination with a solid resin to increase the tack properties.

Suitable plasticizers for use in preparing the hot melt adhesive compositions of the present invention include plasticizing oils like low aromatic content hydrocarbon oils that are paraffinic or naphthenic in character (carbon aromatic distribution ≤5%, preferably ≤2%, more preferably 0% as determined according to DIN 51378). Those products are commercially available from the Royal Dutch/Shell Group of companies, like SHELLFLEX, CATENEX, and ONDINA oils. Other oils include KAYDOL oil from Witco, or TUFFLO oils from Arco. Other plasticizers include compatible liquid tackifying resins like REGALREZ R-1018. (SHELLFLEX, CATENEX, ONDINA, KAYDOL, TUFFLO and REGALREZ are trademarks).

Other plasticizers might also be added, like olefin oligomers; low molecular weight polymers (≤30,000 g/mol) like liquid polybutene or liquid polyisoprene copolymers, like liquid styrene/isoprene copolymers or hydrogenated styrene/isoprene copolymers and liquid alpha-olefin polymers; vegetable oils and their derivatives; or paraffin and microcrystalline waxes.

The preferred plasticizers useful in the present invention are for example, CATENEX N956, CATENEX S946, or EDELEX 945.

The composition according to the present invention may, but need not, contain a plasticizer. If it does, then the composition comprises up to 100 parts by weight, preferably 5 to 75 parts by weight, more preferably 10 to 40 parts by weight of a plasticizer.

Several types of antioxidants can be used, either primary antioxidants like hindered phenols or secondary antioxidants like phosphite derivatives or blends thereof. Examples of commercially available antioxidants are IRGANOX 565 from Ciba-

Geigy (2.4-bis-(n-octylthio)-6-(4-hydroxy-3,5-di-tertiary-butyl anilino)-1,3,5-triazine), IRGANOX 1010 from Ciba-Geigy (tetrakis-ethylene-(3,5-di-tertiary-butyl-4-hydroxy-hydrocinnamate)methane), IRGAFOS 168 from Ciba-Geigy or POLYGARD HR from Uniroyal (tris-(2,4-di-tertiary-butyl-phenyl)phosphite). Other antioxidants developed to protect the gelling of the polybutadiene segments can also be use, like the SUMILIZER GS from Sumitomo (2[1-(2-hydroxy-3,5-di-ter-pentylphenyl)ethyl)]-4,6-di-tert-pentylphenylacrylate); SUMILIZER T-PD from Sumitomo (pentaerythrythyltetrakis(3-dodecylthiopropionate)); or mixtures thereof. (IRGANOX, IRGAFOS, POLYGARD and SUMILIZER are trademarks).

The antioxidant which can be used in the present invention are IRGANOX 1010, IRGANOX 3052, IRGAFOS 168, SUMILIZER GS, SUMILIZER TPD. Extensive research has revealed that optimized antioxidant packages are a combination of IRGANOX 1010/IRGANOX 3052/IRGAFOS 168 or a combination of SUMILIZER GS/SUMILIZER TPD which gave stable hot melts at 180°C.

It should be noticed that the lists of additives disclosed hereabove are merely examples and are not limitative.

Test methods have been performed on the adhesives in order to evaluate those of the present invention which are able to compete with acrylic tapes.

These tests are:

1) Hot melt viscosity stability

Brookfield hot melt viscosity (HMV) at 170°C during 24 hours

2) Gel content

Gel content on adhesive before (ini) and after HMV measurement (24 hrs) on 50µ filter

3) Tack property

Rolling Ball Tack (RBT)

4) Test on cardboard

HP40°C, 1kg weight

Plap test, 500g weight

These tests have shown that in order to attain the object of the present invention, the adhesive composition of (poly(styrene-butadiene-styrene) polymers having a high vinyl content in the butadiene blocks based packaging tapes) ideally should fulfil the following requirements:

RBT:	1-5 cm	(acceptable < 20 cm)
Flap test:	120-250 minutes	(acceptable > 100 minutes)
HP40°C:	50-100 minutes	(acceptable > 40 minutes)
HMV	< 100 Pa.s.	

The tests have been performed with the following polymers A to H, whereby A to F are comparative examples while G and H are embodiments of the present invention.

Table 1

	A	B	C	D	E	F*	G	H
Step I (mol/kg)	11,300	**11,800**	11,100	**11,600**	11,100	10,004	9,100	9,100
Step III (mol/kg)	193,000	223,800	205,300	222,900	199,800	188,400	182,100	175,200
CE (%)	65.5	82.6	**53.8**	**17.6**	**23**	79	67	67
vinyl (%)	40.5	**7.6**	36	**9.2**	55	30	32	33.6
PSC (%)	18.7	17.9	17.9	17.5	18.8	19	18	16
MFR 200°C, 5 kg	3.0					5	14	10

* An example in accordance with EP 0 243 956

The properties are shown in Table 2. In that table, the formulation 1 is a general formulation.

Table 2

Polymer	A	B	C	D	E
Form. 1					
HMV@170, Pa.s	**57**	198	**51**	**26**	**33**
RBT (cm)	**15**	**3**	**6**	**1**	21
HP kraft@40°C, min	**41**	8	9	2	4
Flap kraft@23°C,min	**548**	**118**	82	22	**148**

Form. 1 = 100phr SBS polymer / 125phr HERCOTAC 205 / 40phr CATENEX N956 / 1phr IRGANOX 1010 / 1phr IRGANOX 3052/1phr IRGAFOS 168
It is to be pointed out that in the formulation 1 the amount of the plasticizer CATENEX™ N 956 (40 phr) is too high and this causes bleeding and migration of the adhesive.

Although the formulation based on polymer A exhibits an acceptable balance of properties, this formulation is not acceptable as polymer A has a too low melt flow rate (MFR < 10).

Since formulations with lower oil contents are preferred, for example below 20 phr, polymers with lower step I (MW) have been compared to polymers A to E. These polymers are F, G and H in table 1 and the characteristics of these polymers are indicated in that table 1.

Table 3

In another text a formulation 2 is prepared with the SBS polymers F and G, but containing only 20 phr of the plasticizer CATENEX™ N 956.

Form 2: 100 phr SBS polymer / 125phr HERCOTAC™ 205 / 20 phr CATENEX™ N956 / 1phr IRGANOX™ 1010 / 1phr IRGANOX™ 3052 / 1phr IRGAFOS™ 168

The results of the text are shown hereunder.

	F	G
HMV@170, Pa.s	190	**63**
RBT (cm)	**5**	27
HP kraft@40°C, min	**51**	19
Flap kraft@23°C,min	**708**	**135**

It will be seen that F, having a maximum step I MW of more than 10,000, and a maximum coupling efficiency value of 79% and a MFR of 5, results in a far too high HMV (hot melt viscosity) for a packaging tape formulation rendering it hardly processable so that G is the polymer with the best balance of properties.

It should be pointed out that the properties of the adhesives can be further improved in optimizing the formulation. The most suitable molecule is specified by the parameters hereunder which result in a MFR of 10.

The target molecule has the following characteristics:

Step I (kg/mol)	about 9500
vinyl (%)	about 30
PSC (%)	about 19
CE (%)	about 70

In the following tables, examples are shown where one can see how the properties of the adhesive composition can be altered by changing the amounts of the several additives. In table 4 has been used the polymer G and in table 5 has been used the polymer H.

Table 4

Ingredients	F1A	F1B	F2A	F2B	F3	F4
Polymer G	100	100	100	100	100	100
HERCOTAC 205	125	125	83	83	94	-
PICCOTAC 212	-	-	42	42	46	-
MBG223	-	-	-	-	-	140
CATENEX N956	20	20	20	20	30	30
I1010/I3052/I168	3*1	3*1	3*1	3*1	3*1	3*1
Coating weight, µ	17	24	18	25	18	20
HMV, 170°C, (ini) Pa.s	**63**	**63**	**61**	**61**	**40**	**40**
RBT, cm	27	**5.5**	>30	>30	>30	**7**
HP kraft@40°C, min	19	**27**	**31**	**55**	**30**	**31**
Flap kraft@23°C,min	135	**230**	**308**	**681**	**221**	**179**

3*1 means 1/1/1

Table 5

	F1	F2	F4	F5	F6	F7
Polymer H	100	100	100	100	100	100
HERCOTAC 205	125	105	112.5	100	125	125
PICCOTAC 212	-	-	12.5	25	-	-
CATENEX N956	20	15	20	20		
CATENEX S946					20	
EDELEX 945						20
I1010/I168/I3052	3*1	3*1	3*1	3*1	3*1	3*1
Coating weight, µ	18	18	20	20	19	19
HMV(ini), 170°C, Pa.s	**100**	120	**100**	**90**	**100**	**80**
RBT, cm	29	24	24	30	**15**	25
HP kraft@40°C, min	26	**36**	**39**	**31**	**37**	**33**
Flap kraft@23°C,min	**217**	**239**	**311**	**383**		**239**

It is seen in Table 4 that the compositions F1B and F4 furnish very valuable adhesives falling within the limits of properties desired for the adhesives of the present invention.

Various changes can be made in the above compositions, and products without departing from the scope of the appended claims.

26. 03. 2002

Claims:

(65)

1. Poly(styrene-butadiene-styrene) polymer having a high vinyl content in the butadiene block comprising in combination

i) a polystyrene content (PSC) within a range of 15-20% by weight

ii) a coupling efficiency (CE) of 50-80%

iii) a step I (MW) between 9000 and 10000 kg/mol

iv) a vinyl content between about 20-45%

2. The polymer according to claim 1 wherein the polystyrene content (PSC) is within a range of 16-19% by weight, preferably 16-18% by weight.

3. The polymer according to claim 1 wherein the coupling efficiency is within a range of 60-75%, preferably 65-70%.

4. The polymer according to claim 1 wherein the vinyl content amounts to 25-40% preferably 30-35 by weight.

5. Hot melt adhesive composition comprising:

a) a poly(styrene-butadiene-styrene) polymer having a high vinyl content in the butadiene block

b) a tackifying resin

c) a plasticizer

d) an anti-oxidant

characterized in that said polymer has:

i) a polystyrene content (PSC) within a range of 15-20% by weight

ii) a coupling efficiency (CE) of 50-80%

iii) a step I (MW) between 9000 and 10000 kg/mol

iv) a vinyl content between 20-45%

6. The hot melt adhesive composition according to claim 5 characterized in that said polymer has the following characteristics

Polystyrene (PSC) content (%)	about 19
CE (%)	about 70
Step I (MW) (kg/mol)	about 9,500
Vinyl (%)	about 30

7. The hot melt adhesive composition according to any one of claims 5 to 6 having

a) hot melt viscosity at 170°C during 24 hours lower than 100 Pa.S
b) Rolling back tack: 1-5 cm
c) Flap test, 500 g weight: higher than 120 minutes
d) HP 40°C, 1 kg weight: higher than 50 minutes.

8. The hot melt adhesive composition according to anyone of claims 5-7 wherein the amount of tackifier in the composition comprises 50 to 200 parts by weight, preferably 100 to 150 parts.

9. The hot melt adhesive composition according to anyone of claims 5-8 wherein the amount of plasticizer in the composition is up to 100 parts by weight, preferably 5 to 75 parts by weight.

Abstract

The present invention concerns a poly(styrene-butadiene-styrene) polymer having a high vinyl content in the butadiene block comprising in combination a polystyrene content (PSC) within a range of 15-20% by weight, a coupling efficiency (CE) of 50-80%, a step I (MW) between 9000 and 10000 kg/mol, a vinyl content between about 20-45%.

Hot melt adhesive compositions are also described comprising said SBS polymer together with a tackifying resin, a plasticizer, an anti-oxidant.

EPO - DG 1

26. 03. 2002

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